

Catalysis at the NSLS: Importance of Oxygen Vacancies in the Behavior of Oxide Catalysts

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Introduction

Metal oxides are widely used as catalysts in environmental chemistry and commercial processes that deal with the conversion of hydrocarbons [1]. Thus, oxide catalysts are useful in the destruction of the SO₂ and NO_x species produced during the combustion of fuels in automobiles, factories and power plants. By preventing the emission of SO₂ and NO_x into the atmosphere, they help to minimize the negative effects of acid rain on the environment [1,2]. Selective oxidation, ammoxidation, and dehydrogenation probably constitute the most important industrial applications of oxide catalysts active for the conversion of hydrocarbons [1]. Each year these processes produce millions of dollars in revenues.

Over the years there has been a considerable interest in obtaining a fundamental understanding of phenomena responsible for the good performance of oxide catalysts [1,3,4]. Part of the problem in explaining the behavior of these systems arises from the fact that they are complex and very difficult to characterize, in many cases containing several interacting phases and

a small fraction of active sites [1]. Useful knowledge in this subject can be obtained through synchrotron based techniques, which nowadays allow the detailed study of the interaction of molecules with surfaces (photoemission, x-ray absorption spectroscopy, infrared spectroscopy, etc) or the evolution of catalytic materials under reaction conditions (x-ray diffraction and scattering, extended x-ray absorption fine structure, etc) [5-8]. These techniques become particularly powerful when combined with state-of-the-art density function (DF) calculations [9]. Using such an approach, recent studies carried out at the NSLS (U7A, X7B, X16C, X19A beamlines) have shown the importance of oxygen vacancies in the behavior of oxide catalysts [10-14].

DeSOx and DeNOx reactions on Titania

Titania (TiO₂) is used as a catalyst/sorbent for the Claus reaction ($\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + \text{S}_{\text{solid}}$) and the destruction of NO_x species [10,13]. High-resolution photoemission (U7A beamline) has been used to study the

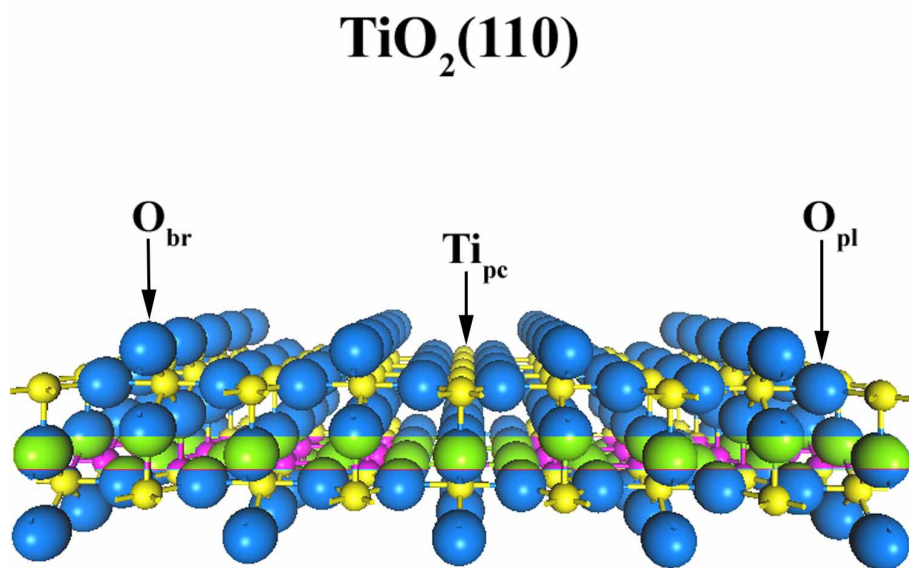


Figure 1. A perfect TiO₂(110) surface. The O atoms are represented as blue spheres, while yellow spheres denote Ti atoms.

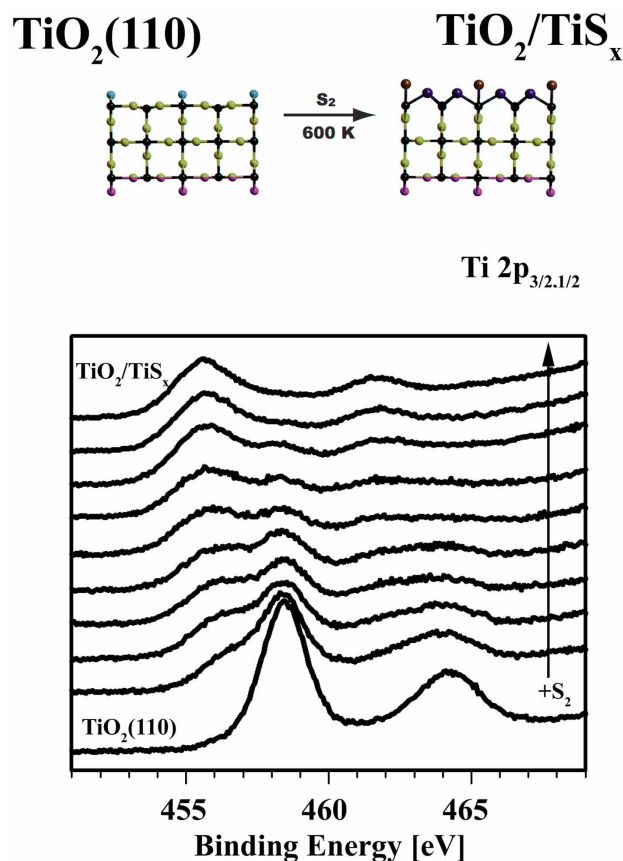


Figure 2. Ti 2p core level photoemission spectra for the reaction of sulfur with a $\text{TiO}_2(110)$ surface at 330 °C [11]. Photon energy = 625 eV

interactions of S_2 , SO_2 , NO, N_2O and NO_2 with a $\text{TiO}_2(110)$ surface [10,11,13,14]. Figure 1 shows the structural geometry of this surface. In a perfect $\text{TiO}_2(110)$ surface, adsorbates can interact with pentacoordinated Ti sites (Ti_{pc}) or atoms in the O bridging rows (O_{br}). In addition O vacancies can be present in the O bridging rows or the bulk of the oxide sample [10,13]. Photoemission data and first-principles DF calculations indicate that these vacancies play a dominant role in the chemical properties of the $\text{TiO}_2(110)$ surface [10,11,13]. When present on the surface they offer adsorption sites which are more reactive than Ti_{pc} or O_{br} sites [10,11,13]. Furthermore, the exchange of O vacancies between the surface and bulk of the sample can lead to unexpected chemical transformations [11,13]. Figure 2 shows Ti 2p core-level spectra for the adsorption of S_2 on $\text{TiO}_2(110)$ at 330 °C [11].

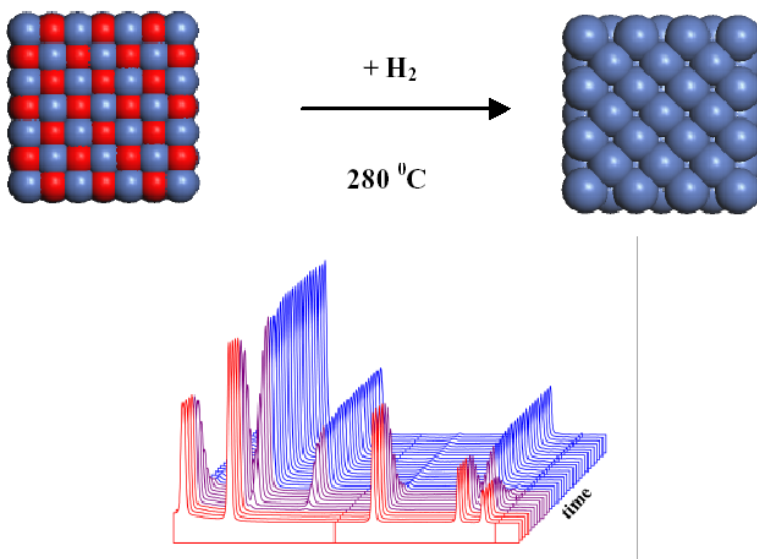


Figure 3. Time-resolved x-ray diffraction results for the reaction of a NiO powder with H_2 at 280 °C [14]. X axis is 2θ , Y axis is time, and Z is intensity.

As sulfur is dosed, the peaks for TiO_2 completely disappear and new features appear for titanium sulfide. There is a complete $\text{TiO}_2 \rightarrow \text{TiS}_x$ transformation in the surface and near subsurface regions. This is surprising since oxides are much more stable than sulfides and a $\text{S}_2(\text{gas}) + \text{TiO}_2 \rightarrow \text{TiS} + \text{SO}_2(\text{gas})$ reaction does not occur on the surface [11]. The key to the $\text{TiO}_2 \rightarrow \text{TiS}_x$ transformation is a S induced migration of O vacancies from the bulk of the oxide to the surface [11]. Adsorbates like Au and NO_x species can also induce a migration of O vacancies in TiO_2 , thus producing an important enhancement in the chemical reactivity of this oxide surface [11-13].

Reduction in Hydrogen and Activation of Oxide Catalysts

In most cases, pure stoichiometric oxides do not exhibit high catalytic activity [1]. One method frequently employed for the preparation of active oxide catalysts consists of partial reduction under hydrogen at elevated temperatures [1]. In this process, it is important to identify well-defined suboxides that can have high catalytic activity and are stable at the elevated temperatures typical of many catalytic reactions [1,11]. Experiments at beamline X7B have shown that *in situ* time-resolved x-ray diffraction is a powerful technique to study the reduction/activation of oxides [11,15]. Figure 3 displays time-resolved XRD data for the reaction of hydrogen with a NiO powder at 280 °C [14]. During the first 50 min, no major changes are seen in the intensity of the diffraction lines for NiO (in red). The NiO lines then begin to disappear, and simultaneously lines for metallic Ni

appear (in blue), without any well-ordered intermediate phase. An induction or delay time was also found in photoemission experiments (U7A) for the reduction of a NiO(100) single-crystal, in NEXAFS/EXAFS measurements (X16C) for the reduction of NiO powder [14], and in time-resolved XRD data (X7B) for the reduction of cobalt and nickel molybdates [15]. Thus, such phenomenon must be taken into consideration when aiming at the activation of oxides via reduction in hydrogen.

In Figure 3, it could be argued that the induction time is associated with the formation of an amorphous NiO_x phase with special chemical properties. This possibility was ruled-out after analyzing NEXAFS/EXAFS data (Figure 4, for example) using the principal-component-analysis (PCA) method. The PCA results indicated that only two components (NiO initial phase, Ni final phase) were present in the system [14]. *Photoemission and DF results for the adsorption of H₂ on NiO(100) indicate that O vacancies play a key role during the induction time, generating the necessary sites for the dissociation of the adsorbate.* A perfect NiO(100) surface, the most common face of nickel oxide, exhibits a negligible reactivity towards H₂ [14].

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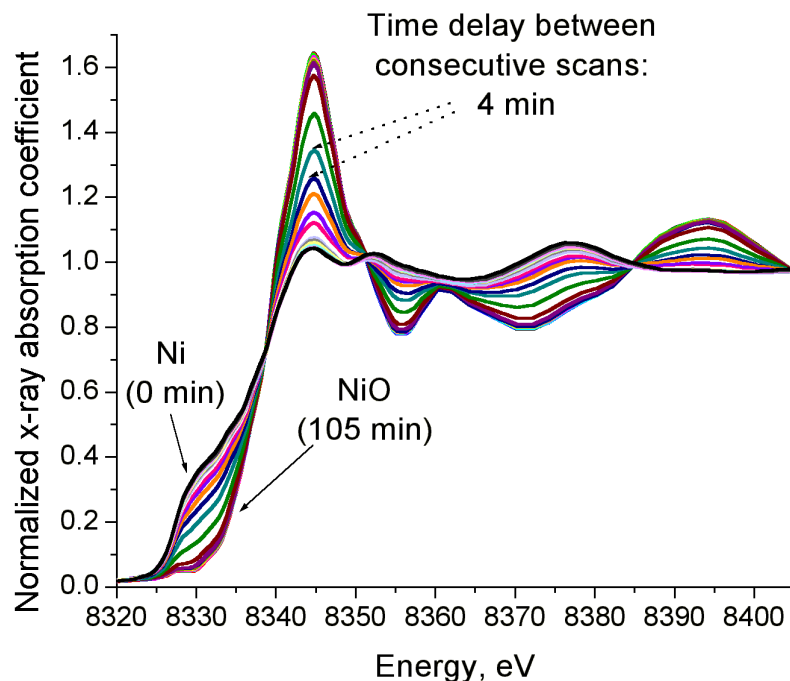


Figure 4. Time-resolved edge-step normalized NEXAFS data for the reduction of NiO powder at 280 °C under a flow of hydrogen [14].